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The Hydrazone Formation

with Oxomalonic Esters

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**THE HYDRAZONE FORMATION WITH OXOMALONIC ESTERS**

**BY**

**CHARLES KAY HEWES**

**THESIS**

**FOR THE**

**DEGREE OF BACHELOR OF SCIENCE**

**IN**

**CHEMICAL ENGINEERING**

**COLLEGE OF SCIENCE**

**UNIVERSITY OF ILLINOIS**

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Charles Kay Hewes

ENTITLED The Hydrazone Formation with Oxomalonic Esters

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in

Chemical Engineering

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Instructor in Charge

APPROVED:

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Chemistry

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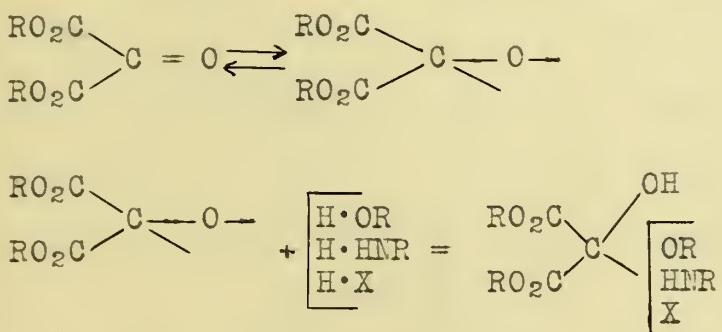
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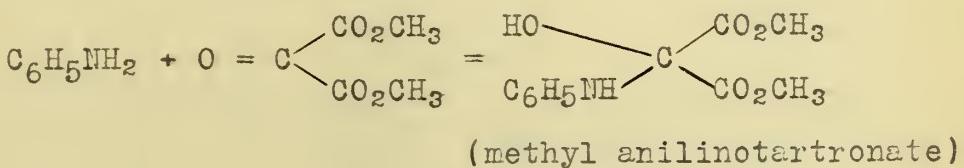
## THE HYDRAZONE FORMATION WITH OXOMILLONIC ESTERS.

## Introduction.

The oxomalonic esters unite very readily with substances containing a dissociable hydrogen atom, the latter uniting with the oxygen of the carbonyl group and the remainder of the molecule combining directly with the carbon atom of the carbonyl group. Curtiss and Spencer<sup>1</sup> have prepared a series of compounds by the reaction of substances of the general type H·OR, H·HNR, and H·X on the ethyl and methyl esters of oxomalonic acid, O = C = (CO<sub>2</sub>R)<sub>2</sub>.



It was found that the reactivity of the ethyl keto-ester is greater than that of the methyl. For example, Curtiss and Spencer<sup>2</sup> obtained an addition product when equal mols of aniline and methyl oxomalonate were mixed.

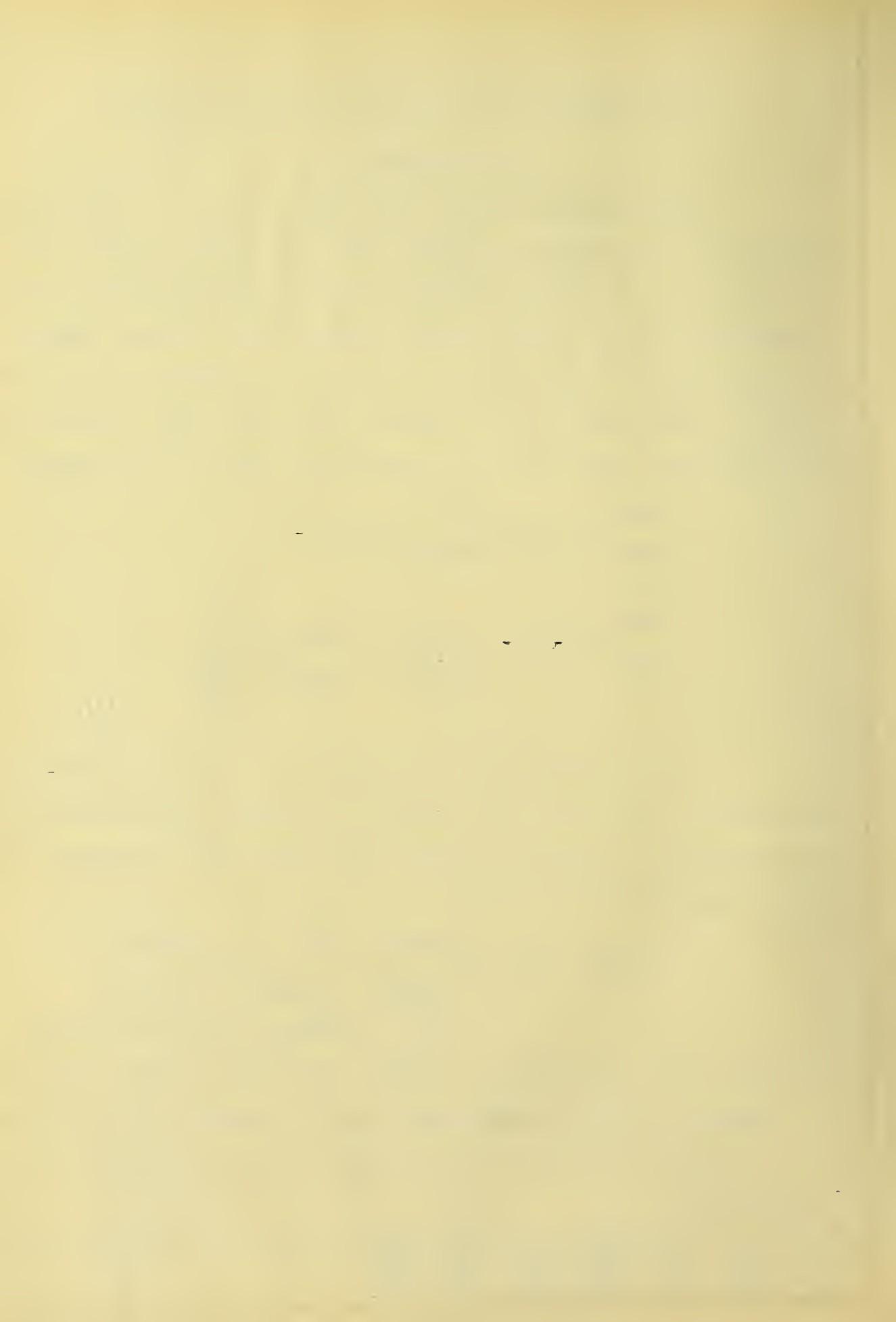


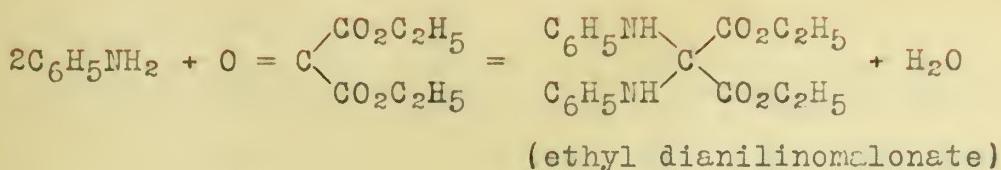
When the ethyl oxomalonate, however, was tried Curtiss<sup>3</sup> was unable to separate out the intermediate addition product, but found that two molecules of aniline were required to unite with one of the oxomalonate.

Jour. Amer. Chem. Soc., 31, 1053.

2. Jour. Amer. Chem. Soc., 31, 1053.

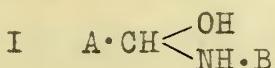
3. Jour. Amer. Chem. Soc., 35, 354.





Curtiss, Hill, and Lewis<sup>4</sup> studied the behavior of the three toluidines, aniline, and benzylamine on ethyl oxomalonate with the intent of obtaining the hypothetical intermediate addition products. They obtained products of the form  $\begin{array}{c} RNH \\ | \\ HO \\ | \\ CO_2C_2H_5 \\ | \\ CO_2C_2H_5 \end{array}$  i.e. substituted aminotartronates for all but aniline. This gave the dianilinomalonate as stated above.

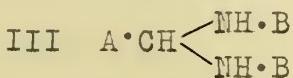
In the case of the action of primary amines on aldehydes and ketones considerable work has been done. Rügheimer<sup>5</sup> explains the formation of the different compounds. Considering the formula of the aldehyde as  $A \cdot C=O$  and the amine as  $B \cdot NH_2$ , in every case the first product of the reaction is a compound of the formula



If the union of the hydroxyl group and carbon atom is not very strong, water splits out with the formation of



If, however, this union is stronger there is a possibility of the formation of the compound



Thus it is possible to pass from I to II or III and in the following review of some of the addition compounds of primary amines on aldehydes and ketones, this property will be noticed. In many cases the primary addition product I is so unstable that it

4. Jour. Amer. Chem. Soc., 35, 400.

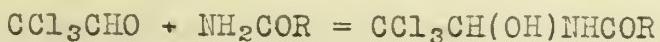
5. Ber. d. Deu. Chem. Gesell., 39, 1653.



cannot be separated out.

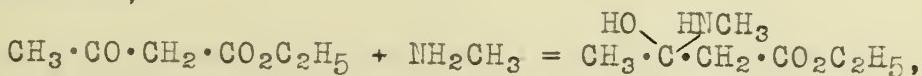
The amides have been found to react in a manner analogous to the amines, that is, to give the intermediate addition products. As early as 1870 Jacobsen<sup>6</sup> obtained the addition products of acetamide, benzamide, and urea on chloral. All were stable up to 150° - 160°.

In like manner Görtner<sup>7</sup> separated out a series of addition compounds that were formed in the reaction of chloral and amides of the type  $\text{NH}_2\cdot\text{CO}\cdot\text{R}$



Schiff<sup>8</sup> has prepared  $\text{CCl}_3\cdot\text{CH(OH)NH}\cdot\text{C}_2\text{H}_3\text{O}$  (chloral acetyl) and  $\text{CCl}_3\cdot\text{CH(OH)NH}_2$  (chloral ammonia). The author came to the conclusion that the above structures were correct after having obtained the acetyl derivatives on the hydroxyl group.

In the reaction of alkylamines on acetacetic ester Kuckert<sup>9</sup> obtained the primary addition product in the case of the methyl amine,



but got no intermediate product with the diethylamine. In the above compound water splits out easily to give the  $-\text{N}=\text{C}=$  group or a tautomeric form.

Several addition products have been made with benzaldehyde, Hantzsch and Kraft<sup>10</sup> obtained the product with m benzoic acid, Hantzsch and Schwab<sup>11</sup> with p chlor- and p bromanilines, and

6. Ann. der Chem., 157, 243.

7. Ann. der Chem., 532, 226.

8. Ber. d. Deu. Chem. Gesell., 10, 165.

9. Ber. d. Deu. Chem. Gesell., 18, 618.

10. Ber. d. Deu. Chem. Gesell., 24, 3521.

11. Ber. d. Deu. Chem. Gesell., 24, 830.



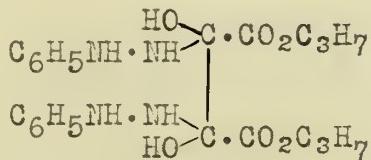
Dimroth and Zeeppritz<sup>12</sup> with p nitraniline.

In the reaction of aniline on benzaldehyde Rügheimer<sup>13</sup> states that the intermediate product is very unstable but the compound  $C_6H_5CH = NC_6H_5$  is quite stable. He also prepared the addition products of chloral on 1·3·4 toluylendiamine,  $\alpha$  naphtylamine,  $\beta$  naphtylamine, aniline,  $\alpha$ -phenylenediamine,  $p$ -phenylenediamine, and  $p$ -toluidine.

Wheeler and Jordan<sup>14</sup> state that the chloral condensation products with aniline and the toluidines are less stable than with those containing one or two negative atoms or groups substituted in the benzene ring. They prepared the addition products with 2 nitro 4 toluidine and 3 chlor 4 toluidine.

With aniline,  $p$ -toluidine, and  $p$ -nitroaniline on chloral Eibner<sup>15</sup> obtained addition products of the form  $CCl_3 \cdot CH(OH)NH \cdot R$ . By heating above the melting point, these compounds readily pass over to the diphenylamine unions,  $CCl_3 \cdot CH(NH \cdot R)_2$ .

Anschütz and Pauly<sup>16</sup> prepared the intermediate product in the reaction of phenylhydrazine on the propyl ester of dioxo-succinic acid. The compound has the formula



- 12. Ber. d. Deu. Chem. Gesell., 35, 986.
- 13. Ber. d. Deu. Chem. Gesell., 39, 1653.
- 14. Jour. Amer. Chem. Soc., 31, 937.
- 15. Ann. der Chem., 302, 362.
- 16. Ber. d. Deu. Chem. Gesell., 28, 67.



The action of phenylhydrazine on oxaloacetic ester was tried by Wislicenus and Scheidt<sup>17</sup> and the addition compound  $\text{CO}_2\text{C}_2\text{H}\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{C}_2\text{H}_5$  was obtained. This compound was found to be very unstable and readily passed over to the hydrazone,  $\text{CO}_2\text{C}_2\text{H}_5\cdot\text{C}(\text{NH}\cdot\text{C}_6\text{H}_5)\cdot\text{CH}_2\cdot\text{CO}_2\text{C}_2\text{H}_5$ .

In the field of the oxomalonate esters, several examples of the addition products have been met with. Curtiss and Strachan<sup>18</sup> obtained the addition compound with urethan and methyl oxomalonate. As has been mentioned above Curtiss, Hill, and Lewis<sup>19</sup> obtained the primary addition products with the toluidines and ethyl oxomalonate. Difficulty was encountered when an attempt was made to split off the elements of water in order to give the  $-\text{N}=\text{C}=$  bond.

With aniline and methyl oxomalonate Curtiss and Spencer<sup>20</sup>, as already stated, obtained the methyl anilinotartronate,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{C}(\text{OH}):(\text{CO}_2\text{CH}_3)_2$ , as a comparatively stable compound.

Mandel<sup>21</sup> prepared an addition compound of aminoazobenzene on methyl oxomalonate,  $\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}(\text{OH}):(\text{CO}_2\text{CH}_3)_2$ .

In regard to the constitution of these various addition compounds on ketones and aldehydes, considerable discussion appeared in the earlier literature on the subject. Of the two possible structures for these compounds,  $\text{C}(\text{OH})\text{—NH}_2$  and  $\text{C}(\text{NH}_2)\text{—O—}$ , Wislicenus and Beckh<sup>22</sup> showed that the latter might hold for such compounds as the addition product of oxaloacetic ester and phenylhydrazine that is decomposed into its components by means of sodium hydroxide or mineral acids. The fact, though, that dioxosuccinic

17. Ber. d. Deu. Chem. Gesell., 24, 3006.

18. Jour. Amer. Chem. Soc., 33, 397.

19. Jour. Amer. Chem. Soc., 33, 400.

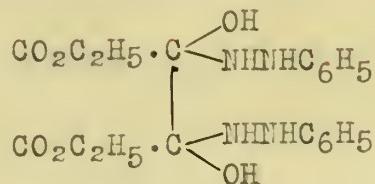
20. Jour. Amer. Chem. Soc., 31, 1057.

21. Thesis, University of Illinois, 1912.

22. Ber. d. Deu. Chem. Gesell., 28, 788. Ann. der Chem., 295, 339.



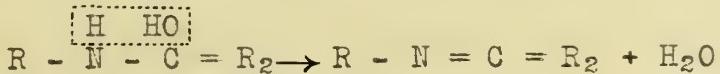
ester yields an addition product with phenylhydrazine,



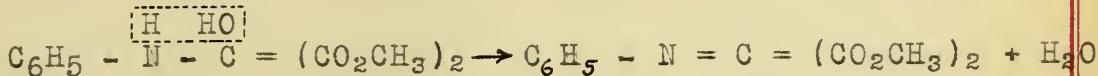
argues for the former structure because it is not possible to write this compound as an ammonium salt.

#### The Hydrazone Formation with Oxomalic Esters.

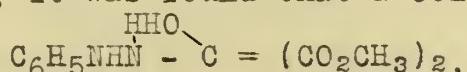
The object of our investigation was to study the behavior of the hydrazines on the reactive keto-esters of oxomalic acid and if possible, to isolate any intermediate addition products that may be formed in the reaction. The addition compounds, considered as the primary addition product of an amine on a keto group, might be expected to lose water readily and give the  $\text{-N}=\text{C}=$  group that is typical of the usual final reaction product of a substituted amine on ketone and aldehyde groups.



This was found to be the case with such derivatives as methyl anilinotartronate mentioned above.



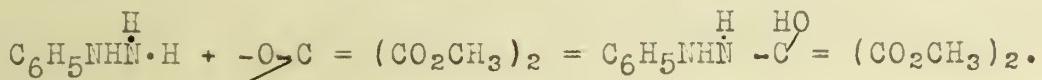
In the reaction of equal mols of methyl oxomalonate and phenylhydrazine, when carefully controlled within a certain temperature limit, it was found that a colorless addition product,



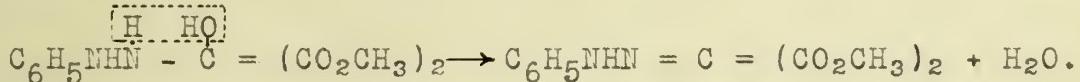
methyl phenylhydrazinotartronate, was formed and could be separated out in the form of a comparatively stable substance.



The dissociable hydrogen atom of phenylhydrazine,  $\text{H}\cdot\text{HNHNC}_6\text{H}_5$ , unites with the free bond of the oxygen atom of the nascent carbonyl group  $-\text{O}=\text{C}$  of methyl oxomalonate and the nascent nitrogen bond unites with the free carbon bond of the carbonyl group.



The white methyl phenylhydrazinotartronate so formed easily splits out water and gives a canary yellow phenylhydrazone as the final product in the typical hydrazone formation.

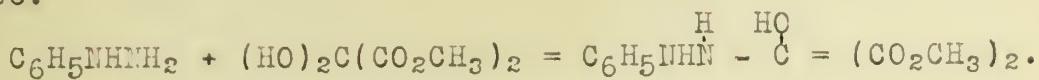


The course of the reaction of phenylhydrazine on methyl oxomalonate is easily followed by the color changes. The green ketone oil containing the chromophore group,  $-\overset{\text{O}}{\text{C}}-\overset{\text{O}}{\text{C}}-\overset{\text{O}}{\text{C}}-$ , soon loses its color by reason of the addition of phenylhydrazine on the central nascent carbonyl group and the consequent loss of the chromophore. After the elimination of the elements of water there results a canary yellow phenylhydrazone that contains the chromophore group  $-\overset{\text{O}}{\text{C}}-\overset{\text{N}}{\text{C}}-\overset{\text{O}}{\text{C}}-$ .

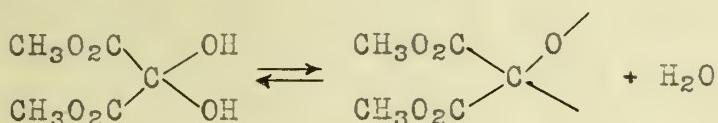
The delicacy of the reaction of methyl oxomalonate and phenylhydrazine to form an intermediate addition product is important. A change of a few degrees in the temperature of the reaction may cause it to go to either the intermediate product or to the final product, the phenylhydrazone. If at the higher temperature a trace of hydrazone is formed that is made evident by the turbidity caused by the dissociated water, this hydrazone or the water seems to act as a catalyst and causes the reaction to go to the hydrazone product.



Methyl phenylhydrazinotartronate was also prepared by the action of equal mols of phenylhydrazine and methyl dihydroxymalonate.



This formation is best explained on the supposition that in a solution of dihydroxymalonate, a small part is in the dissociated  $\text{--O} \rightarrow \text{C} = (\text{CO}_2\text{CH}_3)_2$  form.



The phenylhydrazine reacting on the nascent methyl oxomalonate to form methyl phenylhydrazinotartronate then drives the above reaction to the right to completion.

When equal mols of assymmetric methyl phenylhydrazine,  $\text{C}_6\text{H}_5\text{NHNH}_2$ , and methyl oxomalonate are carefully mixed, a clear reddish oil remains that cannot be made to crystallize. After standing for several hours at room temperature water splits out and forms a layer floating on top of the reddish liquid. The intermediate addition product formed in this reaction is probably too unstable to isolate.

When two mols of assymmetric methyl phenylhydrazine and one of methyl oxomalonate are mixed, a white substance melting at  $109^\circ$  is obtained. It is thought that this is the dihydrazino compound,  $(\text{CH}_3\text{O}_2\text{C})_2\text{C}(\text{NNHCH}_3\text{C}_6\text{H}_5)_2$ , analogous to the union obtained by Wheeler and Weller<sup>23</sup> in the reaction of the nitranilines on chloral. They obtained a product of the structure  $\text{CCl}_3\text{CH}(\text{NHC}_6\text{H}_4\text{NO}_2)_2$ .

Equal mols of naphtylamine,  $\text{C}_{10}\text{H}_7\text{NH}_2$ , and methyl oxomalonate were carefully mixed in an etherial solution. A white



compound melting at 70° was obtained. It is thought that this is the addition compound because of its lack of a chromophore group. This substance will be studied further.

### Experimental.

#### THE ADDITION PRODUCT PRODUCED BY THE REACTION OF PHENYLHYDRAZINE AND METHYL OXOMALONATE.

To one mol (0.81 grams) of phenylhydrazine contained in a 3/4 inch sample tube and an equal volume of sodium dried ether, was added one mol (0.88 cc. or 1.095 grams) of methyl oxomalonate. The latter was added in .01 cc. portions with frequent stirring by means of a thermometer fitted to the tube with a rubber stopper to exclude moisture. At no time was the temperature of the mixture allowed to rise above 75° - 80° and as so much heat was produced in the reaction of the two substances, it frequently was found necessary to cool the mixture in an ice bath. Three minutes were required for the addition of the oxomalonate. A thick, clear, yellowish, solution resulted and it soon changed over to a solid yellow mass. This substance when crystallized from absolute alcohol gave the white methyl phenylhydrazinotartronate, melting at 92° - 93° (uncorrected).

This addition product was found to be somewhat unstable and so far analysis was recrystallized twice from absolute alcohol, was washed well with the same solvent, sucked dry and then put over calcium chloride in a vacuum dessicator for three hours. The results of the analysis are as follows:

I. 0.2028 grams of the substance gave 19.6 cc. nitrogen at 18.5°C and 748.27 mm. pressure.



II. 0.2052 grams of the substance gave 0.3839 grams carbon dioxide and 0.1024 grams water.

Calculated for  $C_6H_5NHN - C = (CO_2CH_3)_2$ ; C, 51.94%; H, 5.55%; N, 11.02%.

Found C, 51.52%; H, 5.63%; N, 11.01%.

Methyl phenylhydrazinotartronate is a white product, its crystals appearing as short, stout, prismatic, needles and arranged in algae structure. It melted at 92° - 93° to a clear colorless liquid, then turned yellow and water was visible in the upper part of the test tube. On cooling a thick yellow oil remained that became crystalline when seeded with a crystal of the phenylhydrazone of methyl mesoxalic ester. When heated to higher temperatures a green distillate and a colorless vapor were obtained. When methyl phenylhydrazinotartronate was treated with acetyl chloride, hydrochloric acid was given off and a clear solution remained. With phenylhydrazine, water split off at a temperature of about 100° and when more heat was applied, the substance decomposed into the green keto oil and phenylhydrazine. Methylphenylhydrazinotartronate is unstable and changes over to the yellow hydrazone. At room temperature the decomposition starts in several days. When kept over sulphuric acid, the white product began to turn yellow in two days and in two months was all changed over to the yellow hydrazone, melting at 61° - 62°. The white product if protected from all light can be kept for a month in an ice box.

Methyl phenylhydrazinotartronate is very soluble in ethyl acetate, easily soluble in benzene, acetone, methyl alcohol, glacial acetic acid, and acetic anhydride, fairly soluble in chloroform and ether, difficultly soluble in carbon tetrachloride,



and nearly insoluble in water and carbon bisulphide.

THE ADDITION PRODUCT PRODUCED BY THE REACTION OF  
PHENYLHYDRAZINE AND METHYL DIHYDROXYMALONATE.

To one mol (1.23 grams) of methyl dihydroxymalonate was added one mol (0.81 grams) of phenylhydrazine. The temperature rose some ten degrees and a thick, canary yellow, liquid was obtained. When seeded with a crystal of methyl phenylhydrazinotartronate it became solid immediately and the temperature rose about fifty degrees. This product crystallized from absolute alcohol and washed well with the same, yielded a pure white compound melting at  $92^{\circ} - 93^{\circ}$  (uncorrected). This is methyl phenylhydrazinotartronate, the same product as is mentioned above in the case of the action of phenylhydrazine on methyl oxomalonate.

A STUDY OF THE TEMPERATURE OF DISSOCIATION OF METHYL  
PHENYLHYDRAZINOTARTRONATE.

An attempt was made to determine the temperature at which complete dissociation takes place of methyl phenylhydrazinotartronate into water and the phenylhydrazone. The experiment was carried out as follows. Dry air was slowly drawn through a U tube containing the substance. This tube was immersed in a paraffin bath and its temperature taken. The water evolved was collected in a calcium chloride tube protected from return moisture from the pump by the use of a sulphuric acid wash bottle. The bath was heated to  $92^{\circ}$  and the temperature was gradually raised. The addition product melted to a clear colorless solution and twenty degrees higher began to turn yellow. Water was noticed in the U tube after heating at  $117^{\circ}$  for seven minutes and this temperature



was maintained for forty minutes. Then the temperature was raised to 125° and kept constant for an hour. Air was drawn through the apparatus for three hours longer. There remained a yellow crystalline phenylhydrazone. The results of the aspiration are as follows:-

Found       $\text{H}_2\text{O}$ , 7.65%; Phenylhydrazone, 91.91%.

Calculated for       $\text{C}_6\text{H}_5\text{NHNHC(OH)}(\text{CO}_2\text{CH}_3)_2$   
 $\text{H}_2\text{O}$ , 7.09%; Phenylhydrazone, 92.91%.

The phenylhydrazone was crystallized from absolute alcohol and analyzed. 0.1253 grams gave 13.4 cc. nitrogen at 21.5° and 734.7 mm. pressure.

Found                          N, 11.81%.

Calculated for  $\text{C}_6\text{H}_5\text{NHN=C}(\text{CO}_2\text{CH}_3)_2$       N, 11.86%.

#### THE ACTION OF ASSYMMETRIC METHYL PHENYLHYDRAZINE ON METHYL OXOMALONATE.

To 2.705 grams (one mol) assymmetric methyl phenylhydrazine and an equal volume of sodium dry ether was carefully added 2.64 cc. (one mol) methyl oxomalonate. The addition was at -12° and extended over a period of five minutes. A clear light yellow, somewhat viscous, liquid resulted that was impossible to crystallize.

When two mols of assymmetric phenylhydrazine were added instead of one and the experiment carried out under the same conditions as just stated, a white crystalline compound was obtained. It was filtered off and washed well with cold ether. The yield was about thirty per cent. The compound melted at 109° to a clear yellow liquid and immediately gave off bubbles of steam. When heated higher the substance decomposed, leaving a thick purplish



black oil.

#### THE ADDITION OF METHYL OXOMALONATE TO $\alpha$ NAPHTYLAMIDE.

One mol (.88 cc.) of methyl oxomalonate and 1.074 grams (1 mol)  $\alpha$  naphtylamine dissolved in 3 cc. sodium dry ether were slowly mixed at -12°. After the ether evaporated a pinkish white substance was obtained that when washed well with absolute alcohol became white and melted at 70° to a clear yellow liquid. The compound seems to be much more stable than any of the others obtained in our investigation.

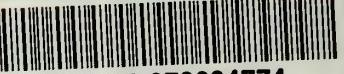
#### THE ADDITION OF METHYL OXOMALONATE TO HYDRAZOBENZENE.

To a small quantity of hydrazobenzene in a small test tube was added a little methyl oxomalonate. Much heat was produced by the reaction and immediately the temperature rose twenty-eight degrees. A thick, clear, light red, liquid formed that when cooled became crystalline.





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